Tetrahedron Letters No.40, pp. 4935-4938, 1966. Pergamon Press Ltd.
Printed in Great Britain.

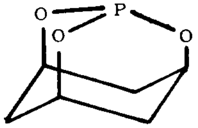
PREPARATION AND SOME REACTIONS OF 2,6,7-TRIOXA-1-PHOSPHA-BICYCLO[2,2,1]HEPTANE (1).

Donald B. Denney and Sandor L. Varga
School of Chemistry
Rutgers, The State University, New Brunswick, New Jersey

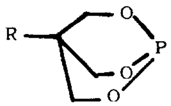
(Received 18 July 1966)

Studies of reactions at bridgeheads of bicyclic systems, where the bridgehead atom is carbon (2) or silicon (3), have proven to be of considerable value in understanding the mechanisms of these reactions and in assessing the role of strain, solvent etc. on the rates of these reactions. Similar studies in other systems, where a different atom is at the bridgehead, can be expected to provide important mechanistic information.

The preparation and some reactions of the two phosphites, I and II, have been reported (4). Qualitative studies have indicated that these substances have different reactivities than the open chain trialkyl phosphites (4a, 5). It is the purpose of this report to describe the synthesis and some qualitative reactivity data of 2,6,7-trioxa-1-phosphbicyclo[2,2,1]heptane, III, and the phosphate, IV, derived from it.

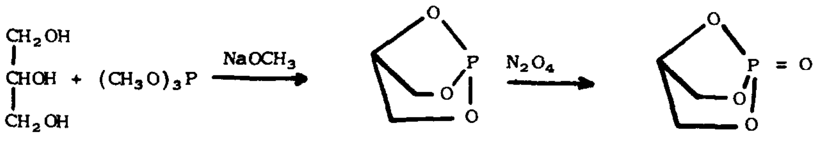


I



II R = CH_3, C_2H_5

Highly purified glycerine (0.5 mole), trimethyl phosphite



III

IV

(0.51 mole) and 50 ml. of SF-96 silicone oil were heated under nitrogen with stirring in an oil bath at 115-120°. Methanol slowly distilled from the reaction mixture. After the rate of distillation slowed considerably, the bath temperature was raised to 140°. When distillation ceased the bath temperature was lowered to 110° and the system was slowly evacuated to 10 mm. to remove the last traces of methanol. The mixture was cooled to 45° and 1.0 g. of sodium methoxide was added. The system was evacuated to 0.25 mm. with constant stirring and at the same time the bath temperature was slowly raised to 125°. The phosphite, III, distilled from the reaction mixture. There was obtained 35.0 g (59%) of crude material. The phosphite is a liquid at room temperature, however it can be purified by crystallization from pentane at -78°. In this manner 24.7 g. of material was obtained. This sample showed only one peak on g.l.p.c. analysis on a Carbowax column at 120°. Anal. Calc'd for $C_3H_5O_3P$: C, 30.01; H, 4.20. Found: C, 30.16; H, 4.24. The molecular weight was found to be 120 (theory 120) by mass-spectrometry (6). The n.m.r. spectrum in acetonitrile consists of two triplets centered at 5.32 and 5.06 p.p.m. and a complex multiplet centered at 3.63 p.p.m. It seems reasonable to conclude that the triplets correspond to the bridgehead hydrogen, which is coupled to phosphorus (J=16 c.p.s.), and to the exo hydrogens (J=3 c.p.s.)

of the methylene groups, but which is only weakly coupled to the <u>endo</u> hydrogens. The relative areas under these peaks are in agreement with these assignments. The infrared spectrum of III is similar to those found for other phosphites; a strong band at 925 cm^{-1} is probably due to P-O-C absorption. These data most adequately fit the structure assigned.

Oxidation of III with nitrogen tetroxide (7) gave a solid phosphate, IV, which was purified by dissolving in methylene chloride followed by precipitation with dry ether. <u>Anal</u>. Calc'd for $C_3H_5O_4P$: C, 26.48; H, 3.71. <u>Found</u>: C, 26.55; H, 3.75. The phosphate does not have a melting point but rather undergoes slow decomposition on heating. The infrared spectrum of IV has the characteristic, P=O, absorption at 1340 cm^{-1} which is also found in the phosphate from II. The n.m.r. spectrum of IV in acetonitrile is similar to that of III with a triplet at 5.41 p.p.m., a highly distorted triplet at 5.00 p.p.m. and a series of peaks between 4.23 and 4.75 p.p.m. The first two absorptions are assigned to the bridgehead hydrogen and the remainder to the methylene hydrogens. The areas under these absorptions are in agreement with this assignment.

Although the chemistry of these materials has not been studied in detail as yet, it has been noted that both are quite unstable to moisture and other hydroxylic media. In particular IV reacts with methanol exothermically and completely in a few minutes. This reactivity is to be contrasted to the phosphate from II which can be recrystallized from ethanol. It has also been noted that III reacts very slowly, incomplete in three months, with benzoyl peroxide while the reaction with trimethyl phosphite is essentially complete in a few hours under the same conditions. Clearly III and IV offer interesting possibilities for study and such work is in progress.

REFERENCES

(1) Research supported by the Public Health Service under GM-12625.

(2) (a) D. E. Applequist and J. D. Roberts, Chem. Rev., 54, 1065 (1954); (b) U. Schollkopf, Angew. Chem. 72, 147 (1960).

(3) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw Hill Book Co., New York, N. Y., 1965, Chap. 9.

(4) (a) W. S. Wadsworth and W. D. Emmons, J. Am. Chem. Soc., 84, 610 (1962); (b) J. G. Verkade and L. T. Reynolds, J. Org. Chem., 25, 663 (1960); (c) H. Stetter and K. Steinacker, Ber., 85, 451 (1952).

(5) S. Varga, unpublished results

(6) We wish to thank Mr. E. Emery and the Colgate-Palmolive Research Center for this determination.

(7) J. R. Cox, Jr. and F. H. Westheimer, J. Am. Chem. Soc., 80, 5441 (1958).